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COMPLETE SPECIFICATION

Phosphorus-Containing Polymers and production thereof

We, TOKYO SHIBAURA ELECTRIC CO. LTD., a corporation organised and existing under the laws of Japan, of 72, Horikawa-cho, Kawasaki-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to phosphorus-containing polymers and to a method of preparing them.

Many heat-resistant and flame-resistant phosphorus-containing polymers have been developed including copolymers of olefins and, for example, triarylphosphine oxides, triarylphosphates, aryl dialkylphosphates or arylphosphonic esters; polyesters of alkyl phosphonic acids; polyphosphonitrile; polymers containing boron-phosphorus bonds; and polymers containing aluminium-phosphorus bonds. The fields of application of these known polymers have, however, been limited to a greater or lesser extent by their relatively high softening point, their resistance to hydrolysis, their brittleness and/or their insolubility in liquid media.

We have now developed a range of phosphorus-containing copolymers which are characterised by excellent flame resistance, heat resistance and self fire extinguishing properties and which can be fused.

According to the present invention, therefore, we provide a copolymer of a phosphine compound of the formula $PX_1X_2X_3$ where X_1 , X_2 and X_3 , which may be the same or different, are halogen atoms or alkyl, aryl, aralkyl, alkenyl, phenoxy, alkoxy, cyano, acyl, cyanate, isocyanate or thiocyanate radicals, provided that all three of X_1 , X_2 and X_3 are not phenoxy or alkoxy radicals and that two of X_1 , X_2 and X_3 are not phenoxy or alkoxy radicals when the third is a halogen atom, and a polymerisable compound containing a terminal double bond.

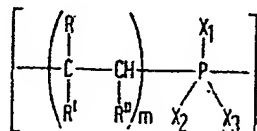
The invention also comprises a method of

preparing these copolymers which comprises copolymerising a phosphine compound of the formula $PX_1X_2X_3$ as defined above, with a polymerisable compound containing a terminal double bond in the presence of an azo compound as polymerisation initiator at a temperature below that at which the resulting copolymer is thermally decomposed.

The phosphine compounds which have been excluded in the above definition are not suitable for use in this invention because they have a tendency to act as telomerisers to form telomers instead of promoting copolymerisation.

Suitable olefinically unsaturated compounds for use as comonomers are, for example, vinylaryl compounds, (such as styrene, p-methylstyrene, o-, m- or p-divinylbenzene, p-chlorostyrene and m-chlorostyrene), α -substituted vinylaryl compounds, allylaryl compounds, and divinylaryl compounds; vinyl compounds such as acrylonitrile, α -substituted acrylonitrile, acrolein, vinyl fatty acid esters, halogenated vinyl compounds, divinyl sulphone, trivinyl phosphine oxide; alkyldivinyl phosphine oxides and aryldivinyl phosphine oxides, acrylic acid, its esters and derivatives such as acrylic amide; α -substituted acrylic acids, their esters and amides; diolefins having conjugated double bonds and allyl derivatives thereof such as halogenated allyl compounds, allyl fatty acid esters, isoprene, butadiene, chloroprene, cyclopentadiene, cyclohexadiene, triallylamine, allyl ester of cyanuric acid, triallylphosphate, and triallyl phosphine oxide; and vinylidene compounds.

The copolymers comprise structural units of the formula:—



where m is an integer equal to or larger than 1, R , R^1 and R^{11} , which may be the same or different, represent the substituents present in the olefinically unsaturated comonomer and are substituted or unsubstituted alkyl, alkenyl, aralkyl, aryl or heterocyclic groups, and X_1 , X_2 and X_3 have the above-stated meaning. While m depends upon the particular monomers used, it is normally preferred that m should not be more than 20 since when m is larger than 20 the polymer tends to lose its useful properties. The average molecular weight of the copolymers is typically from 1500 to 100,000.

In preparing the copolymers it is preferred, as indicated, to use from 1 to 20 moles of the olefinically unsaturated compound per mole of the phosphine compound. Suitable azo compounds for use as polymerisation initiators are, for example, α, α^1 -azobis- α -methylpropylnitrile, α, α^1 -azobis- α -methyl- β -methylbutyronitrile, 2-(2,4-dimethylbenzene diazomercapto)naphthalene, α, α^1 -azobis- α -methyl-capronitrile, 4-(4-methoxybenzene diazomercapto)-anisole, diazoamino-di-4-methoxybenzene, diazoaminobenzene, phenyl azoethane, α, α^1 -azobis- α -cyano- n -valeric acid and 2,2'-azobisisobutyronitrile, but other azobisnitriles, azobis-substituted alkanes, diazothioethers, diazoaminobenzene derivatives and diazonium salts can equally well be used.

The amount of polymerisation initiator employed is suitably from 0.01 to 5% by weight, based on the total weight of the monomers.

It is advantageous to use proportions at the lower end of this range when readily polymerisable olefinically unsaturated compounds, such as diolefins and methacrylic esters, are used and proportions at the upper end of the range when relatively less polymerisable olefinically unsaturated compounds, such as aryl compounds, are used. The amounts of azo initiator may also be relatively small for those phosphine monomers, such as trichlorophosphine and aryl dichlorophosphines, which provide relatively stable phosphine radicals, and relatively large for those phosphine monomers, such as trialkyl phosphines, which yield relative unstable phosphine radicals. In addition where higher reaction temperatures are used, more azo compound is preferably used.

While suitable reaction temperatures vary from case to case, it is advantageous to use a reaction temperature of from -50°C to $+80^\circ\text{C}$, preferably from -20°C to $+60^\circ\text{C}$. Temperatures above 80°C should normally be avoided since such elevated temperatures tend to promote the production of telomers or the homo-polymerisation of the olefinically unsaturated monomer, thus making it difficult to obtain the desired copolymers.

While the reaction proceeds under atmospheric pressure, it is preferable to effect it under a superatmospheric pressure of up to

several hundred kilograms per square centimetre since under higher pressure the polymerisation velocity and conversion ratio are increased. However, when alkoxy substituted phosphine compounds are used, it is necessary to use lower pressures in order to prevent Arbuzov's reaction, that is, a telomerization reaction which tends to occur when an alkoxy-substituted phosphine compound is reacted under pressure with a polymerisable olefinically-unsaturated compound. Care should be taken to maintain the reaction system free from any gas or atmosphere which has a deleterious effect upon the reaction, such as moisture, excessive oxygen, hydrogen, sulphur dioxide, carbon dioxide and carbon monoxide. The reaction is, indeed, preferably carried out in a sealed tube or reaction vessel or under an inert gas, such as helium, nitrogen or argon.

The reaction may be carried out in the absence of any solvent or liquid diluent or in the presence of any solvent which does not promote the production of telomers, such as saturated aliphatic hydrocarbons or aromatic hydrocarbons. The reaction time is, of course, dependent upon such factors as the type and quantity of initiator used, temperature, pressure, the nature of the monomers and the like, and may extend from over five hours to more than one month, including the induction period.

Phosphorus-containing polymers obtained from halogen- or cyano-substituted phosphine monomers are unstable in air but can be rendered stable by dissolving them in a suitable solvent such as acetone or chloromethylene, and then converting them into polyphosphine oxides, polyphosphinic acids or their esters by effecting hydrolysis or alcoholysis in a suitable liquid such as water, aqueous alcohol, alcohol, aqueous dioxane or a mixture of phenol and benzene.

The phosphorus-containing polymers of this invention are also soluble in various solvents such as ketones, halogenated hydrocarbons, esters of acetic acid, phosphoric acid and phosphorus acid. The polymers can therefore readily be formed into films. By proper selection of the phosphine compound, thermosetting type polymers can be obtained by the addition of a cross-linking agent. The polymers are fusible and in the softened or molten state can be extruded, to form films for example, or cast without the necessity for any solvent. The polymers are flame resistant, heat resistant and self extinguishing and, as stated, are fusible and soluble in a variety of solvents so that they have a wide field of applicability. For example, the polymers can be used to make films, tapes, spacers, yarns, filaments, and moulded articles, and can also be used as ion exchange materials.

In order that the invention may be more fully understood, the following examples are given by way of illustration only:—

EXAMPLE 1

A mixture of 0.2 mol of distilled styrene 0.2 mol of distilled phosphorus trichloride free of hydrogen chloride and phosphorus acid was put in a bomb-shaped polymerization vessel which could be sealed by a plug and the air in the vessel was purged with dry oxygen-free nitrogen. After sealing the vessel with the plug, it was immersed in a water bath maintained at 10°C to cool the contents of the vessel. 1.0% by weight of α, α' -azobis- α -methylpropylonitrile was then added to the mixture and the polymerisation vessel was left in the constant temperature water bath for 48 hours to allow polymerisation to take place. At the end of this time, the vessel was removed from the bath, the reaction product was dissolved in acetone, and the solution was poured into cyclohexane to precipitate the polymer. The yield of copolymer was 66% based on the styrene used.

To an acetone solution of the copolymer was added methanol in an amount sufficient to esterify the copolymer but insufficient to precipitate it. After adding one drop of concentrated sulphuric acid to this solution, the mixture was heated under reflux for three hours to effect esterification. After cooling, an excess of methanol was added to the mixture to precipitate the esterified product. After filtration, the esterified product was dried for 24 hours under a vacuum of 1 mm Hg. The results of analysis carried out on the dried product were as follows:—

Infra-red absorption spectrum
 ν max P=O str. = 1235 cm^{-1}
 ν max P=O —CH₂ charac. = 1190 cm^{-1}
 Elemental analysis P = 8.6%
 Reduced specific viscosity: η sp/c = 0.31 (0.5% xylene solution).

EXAMPLE 2

0.3 Mol of distilled acrylonitrile and 0.3 mol of phenyldicyanophosphine (boiling point 144°C/20 mm Hg) were placed in an autoclave and 2.0% by weight of 2-(2,4-dimethylbenzene diazomercapto) naphthalene was added. The air in the autoclave was purged with pure dry nitrogen and the autoclave was sealed with a plug to maintain a pressure of about 10 kg/cm² therein. After allowing the reaction to proceed at room temperature for one week, the reaction product was dissolved in acetone and anhydrous alcohol was added to the solution to precipitate the copolymer. This cycle of dissolving and precipitation was repeated three times to purify the copolymer. The conversion was 95% based on acrylonitrile and the results of analysis were:

Element analysis P = 4.8%
 Reduced specific viscosity η sp/c = 0.55 (0.5% xylene solution).

EXAMPLE 3

A mixture of 0.5 mol of methyl methacrylate free of polymerisation inhibitor, 0.35 mol of phenyldimethylphosphine, 1.5% by weight of di-p-methoxydiazaminobenzene and 50 ml of cyclohexane was sealed in a reaction tube and maintained for 10 days in ice water at 0°C. During this period the catalyst became discoloured and colour of the reaction mixture gradually changed from pale yellow to brownish yellow. After completion of the reaction, the reaction tube was opened, the solid product was removed and dissolved in acetone. The solution was poured into cyclohexane to precipitate the copolymer. The conversion was 72% based on methyl methacrylate and the results of analysis were:

Infra-red absorption spectrum
 ν max P—CH₃ charact. = 1285 cm^{-1}
 Element analysis P = 2.8%
 Reduced specific viscosity: 1.87 (0.5% xylene solution).

EXAMPLE 4

0.42 Mol of divinylbenzene distilled under reduced pressure and 0.9 mol of phenyldimethoxyphosphine were placed in a polymerisation tube which could be sealed by a plug. After cooling in a thermostatic tank maintained at 0°C, 2.0% by weight of α, α' -azobis- α -methylcaplonitrile was added and the air in the tube was purged with dry air-free nitrogen. The tube was then sealed with the plug and left in the thermostatic tank for 10 days to allow polymerisation to take place.

The copolymer precipitate obtained by pouring the viscous liquid obtained by this reaction into petroleum ether, was dissolved in methyl acetate and the methyl acetate solution was poured into methanol to precipitate the copolymer again. The conversion of this reaction as 82% based on the divinylbenzene used and the results of analysis were:—

Infra-red absorption spectrum
 ν max P — O —CH₃ = 11.86 cm^{-1}
 Element analysis P = 3.5%
 Reduced specific viscosity 0.61 (0.5% xylene solution)

As will be clear from these results, even when the reaction was effected with more than 1 mole of phosphine compound per mole of olefinically unsaturated compound, the whole of the phosphine compound did not react to form the copolymer; thus phosphorus-phosphorus bonds were not formed.

EXAMPLE 5

A mixture of 1.0 mol of n-butyl methacrylate and 0.2 mol of triphenylphosphine was dissolved in benzene and the solution was placed in a reaction vessel. After adding 2.7%

by weight of diazoaminobenzene, the air in the reaction vessel was purged with dry nitrogen and the vessel was left in a thermostatic tank maintained at 70°C for 10 hours to allow polymerisation to take place. A viscous brown solution was obtained and this was poured into methanol to precipitate the polymer produced, the separated precipitate was dissolved in acetone and again poured into methanol to purify it.

The product obtained was a glass-like material which is a little more brittle than poly-n-butyl methacrylate, and the results of analysis of this product were:—

- 15 Infra-red absorption spectrum
 $\nu_{\max} \text{ P } -\text{C}_6\text{H}_5 = 1432 \text{ cm}^{-1}$
 Element analysis P = 0.58%

EXAMPLE 6

A mixture of 1.0 mol of vinyl toluene and 0.1 mol of diphenylchlorophosphine was placed in a pressure vessel which could be hermetically sealed. After adding 0.05% by weight of α, α' -azobis- α -methylcaplonitrile, the air in the vessel was replaced by dry nitrogen and the vessel was sealed at a pressure of 12 kg/cm². The vessel was then left in a thermostatic tank maintained at 45°C for 100 hours and a viscous brownish yellow liquid was obtained. The liquid was dissolved in a benzene-methanol mixture and heated under reflux for 15 hours to extract and remove unreacted components. The solvent was then removed to obtain the polymer. This polymer contained chlorine which could not be removed by methanol and ethanol treatment. The results of analysis of this polymer were:—

Infra-red absorption spectrum
 $\nu_{\max} \text{ P } -\text{C}_6\text{H}_5 = 1441 \text{ cm}^{-1}$
 Element analysis P = 0.92%

EXAMPLE 7

A mixture of 1.0 mol of acrylonitrile and 0.005 mol of phosphorus trichloride was placed in a reaction vessel and n-hexane was added to the mixture in an amount sufficient to provide a 50% by weight solution. After adding 0.23% by weight of 2 - (2,4 - dimethyl - benzene-diazomercapto) naphthalene, the mixture was reacted for 12 hours under a stream of dry nitrogen stream while being maintained at 50°C and a white precipitate of copolymer was obtained. This copolymer was heated in alcohol to produce a polymer which was stable against moisture, and the result of the analysis thereof was:—

55 Element analysis P = 0.49%.

EXAMPLE 8

To a mixture of 0.4 mol of styrene and 0.2 mol of phosphorus trichloride was added 0.008 mol (2.7% by weight) of 2,2'-azobisisobutyronitrile and the mixture was reacted

for 72 hours under a stream of dry nitrogen stream while being maintained at 60°C. The viscosity of the reaction mixture increased gradually and it substantially lost its fluidity after about 60 hours although remaining clear and transparent. The final product was a pale yellow transparent glass-like solid. This solid was purified by dissolving it in anhydrous benzene and then pouring the solution into anhydrous cyclohexane or anhydrous n-hexane. Analysis showed that

P = 8.6%.

When a solution of this product in a solvent such as benzene, toluene, chloroform or methylene chloride was hydrolysed by agitating the solution with warm or cold water, a colourless mass of hydrolysed polymer was obtained. By adding a solution of this polymer in benzene to phenol and then dry distilling, the phenyl ester of the polymer was obtained.

EXAMPLE 9

A mixture of 0.2 mol of methyl methacrylate 0.2 mol of phosphorus trichloride and 0.007 mol (2.7% by weight) of 2,2'-azobisisobutyronitrile was maintained at a temperature between -2°C to 2°C for 7 days under a stream of dry nitrogen and a colourless transparent glass-like solid polymer was obtained. The solid polymer was elastic and was purified by dissolving it in anhydrous benzene and re-precipitating it by the addition of dehydrated petroleum benzene to the solution. Like the copolymer with styrene, this purified product could be hydrolysed or esterified by using water, methyl alcohol, ethyl alcohol, butyl alcohol, phenol or the like. The amide form of this product could be obtained by reacting the polymer with amines and the phosphinothiolate ester form by reacting it with mercaptan.

EXAMPLE 10

0.006 mol (1.3% by weight) of 2,2'-azobisisobutyronitrile was added to a mixture of 0.45 mol of vinyl acetate and 0.3 mol of methyl-dichlorophosphine and the mixture was warmed to dissolve the 2,2'-azobisisobutyronitrile completely. The temperature of the mixture was then raised to 40°C under dry air and the mixture was maintained at this temperature for four days to allow the reaction to proceed. 27 g. of a pale yellow transparent glass-like solid polymer were obtained.

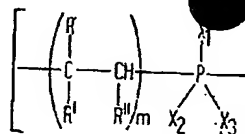
Analysis P = 1.25%.

EXAMPLE 11

A mixture of 0.4 mol of triallylphosphine oxide and 0.1 mol of phenyldichlorophosphine was heated to 50°C to produce a homogeneous solution. After adding 0.01 mol (1.9% by weight) of 2,2'-azobisisobutyronitrile, the solution was placed in a tube. The air in the tube was purged with dry nitrogen for 20 minutes and the tube was sealed. The temperature was then raised to 50°C and maintained at this

level for 24 hours to allow the reaction to proceed and a viscous reaction product was obtained. After distilling off the unreacted components by raising the temperature to 80°C under a reduced pressure of 2 mm Hg, the residue was poured into methanol to give a dough-like copolymer at a conversion of 58% based on the triallylphosphine oxide.

Analysis P=19.7% (after hydrolysis).



where m is an integer from 1 to 20, R , R^1 and R^{11} , which may be the same or different, are substituted or unsubstituted alkyl, alkenyl, aralkyl, aryl or heterocyclic groups, and X_1 , X_2 and X_3 , which may be the same or different, are halogen atoms or alkyl, aryl, aralkyl, alkenyl, phenoxy, alkoxy, cyano, acyl, cyanate, isocyanate or thiocyanate radicals, provided that all three of X_1 , X_2 and X_3 are not phenoxy or alkoxy radicals and that two of X_1 , X_2 and X_3 are not phenoxy or alkoxy radicals when the third is a halogen atom.

6. A copolymer according to claim 1 substantially is herein described in any of the Examples.

7. A method of preparing a phosphorus-containing polymer which comprises copolymerising a phosphine compound of the formula $PX_1X_2X_3$, where X_1 , X_2 and X_3 , which may be the same or different, are halogen atoms or alkyl, aryl, aralkyl, alkenyl, phenoxy, alkoxy, cyano, acyl, cyanate, isocyanate or thiocyanate radicals, provided that all three of X_1 , X_2 and X_3 are not phenoxy or alkoxy radicals and that two of X_1 , X_2 and X_3 are not phenoxy or alkoxy radicals when the third is a halogen atom, with a polymerisable compound containing a terminal double bond in the presence of an azo compound as polymerisation initiator at a temperature below that at which the resulting copolymer is thermally decomposed.

8. A method according to claim 7, in which the olefinically unsaturated compound is a vinylaryl compound, an α -substituted vinylaryl compound, an allylaryl compound, a divinylaryl compound, a vinyl compound, a vinyl fatty acid ester, a halogenated vinyl compound, divinyl sulphone, trivinyl phosphine oxide, an alkyldivinyl phosphine oxide, an aryl-divinyl phosphine oxide, acrylic acid, an acrylic acid ester, acrylic amide, an α -substituted acrylic acid, an α -substituted acrylic acid ester, an α -substituted acrylic acid amide, a diolefin having conjugated double bonds and allyl derivatives thereof, an allyl fatty acid ester, or a vinylidene compound.

9. A method according to claim 7, in which the olefinically unsaturated compound is styrene, p-methylstyrene, o-, m- or p-divinylbenzene, p-chlorostyrene, m-chlorostyrene, acrylonitrile, acrolein, isoprene, butadiene, chloroprene, cyclopentadiene, cyclohexadiene, triallylamine, allyl ester of cyanuric acid, triallylphosphate or triallyl phosphine oxide.

10. A method according to any of claims 7 to 9, in which the initiator is α,α' -azobis-

10 In an alternative procedure, the solution containing the initiator was placed in a high pressure reaction vessel and the air in the vessel was replaced by passing dry nitrogen for 20 minutes. The lid of the reaction vessel was closed and further dry nitrogen was introduced to raise the pressure to about 5 kg/cm². Reaction was then carried out as described above to give the same product.

WHAT WE CLAIM IS:—

1. A copolymer of a phosphine compound of the formula $PX_1X_2X_3$ where X_1 , X_2 and X_3 , which may be the same or different, are halogen atoms or alkyl, aryl, aralkyl, alkenyl, phenoxy, alkoxy, cyano, acyl, cyanate, isocyanate or thiocyanate radicals, provided that all three of X_1 , X_2 and X_3 are not phenoxy or alkoxy radicals and that two of X_1 , X_2 and X_3 are not phenoxy or alkoxy radicals when the third is a halogen atom, and a polymerisable compound containing a terminal double bond.
2. A copolymer according to claim 1, in which the olefinically unsaturated compound is a vinylaryl compound, an α -substituted vinylaryl compound, an allylaryl compound, a divinylaryl compound, a vinyl compound, a vinyl fatty acid ester, a halogenated vinyl compound, divinyl sulphone, trivinyl phosphine oxide, an alkyldivinyl phosphine oxide, an aryl-divinyl phosphine oxide, acrylic acid, an acrylic acid ester, acrylic amide, an α -substituted acrylic acid, an α -substituted acrylic acid ester, an α -substituted acrylic acid amide, a diolefin having conjugated double bonds and allyl derivatives thereof, an allyl fatty acid ester, or a vinylidene compound.
3. A copolymer according to claim 1, in which the olefinically unsaturated compound is styrene, p-methylstyrene, o-, m- or p-divinylbenzene, p-chlorostyrene, m-chlorostyrene, acrylonitrile, acrolein, isoprene, butadiene, chloroprene, cyclopentadiene, cyclohexadiene, triallylamine, allyl ester of cyanuric acid, triallylphosphate or triallyl phosphine oxide.
4. A copolymer according to any of claims 1 to 3 which comprises from 1 to 20 moles of the olefinically unsaturated compound per mole of phosphine compound.
5. A copolymer comprising structural units of the formula:

- methylpropynitrile, α, α' -azobis- α -methyl- β -methylbutylnitrile, 2-(2,4-dimethylbenzene diazomercapto) naphthalene, α, α' -azobis- α -methylcapronitrile, 4(4-methoxybenzene diazomercapto) anisole, diazoamino-di-4-methoxybenzene, diazoaminobenzene, phenylazoethane, α, α' -azobis- α -cyano-n-valeric acid or α, α' -azobis-isobutylnitrile.
- 5 11. A method according to any of claims 7 to 10, in which the amount of initiator used is from 0.01% to 5% by weight based on the total weight of the monomers.
- 10 12. A method according to any of claims 7 to 11, in which copolymerisation is effected at a temperature of from -20°C to $+60^{\circ}\text{C}$.
13. A method according to any of claims 7 to 12, in which copolymerisation is effected under an inert atmosphere.
14. A method according to any of claims 7 to 13, in which the reaction product is hydrolysed and/or esterified.
15. A method of preparing a phosphorus-containing polymer substantially as herein described in any of the Examples.
- 20

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